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## The Function of Bleaching Earths in the Processing of Palm, Palm Kernel and Coconut Oils

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### ABSTRACT

The results presented in the literature, which attempt to elucidate the mechanisms by which triglyceride oils are bleached by earths, are reviewed. The impact of this work and how the mechanistic proposals affect changes in oil properties are considered, with particular emphasis on the needs of the palm oil processor. Important properties include color, metals and phosphorus content and oxidative stability of the oil.

Investigations made in our own laboratories have been aimed at elucidating the effect of varying physical and chemical properties of the bleaching earth on the quality of bleached and deodorized oils. Techniques used in this work are pore-size distribution, surface area, scanning and transmission electron microscopy and a variety of chemical and X-ray analysis methods.

The ability to vary such parameters in montmorillonite clays by alteration of process conditions to give materials with specific performance characteristics is demonstrated.

Comparisons are made between acid-activated montmorillonites and other clay types.

### INTRODUCTION

The use of acid activated montmorillonites in the physical and chemical refining of palm, palm kernel and coconut oils is a widely accepted process (1,2). In this paper, we appraise the current state of knowledge of the way in which bleaching earths function.

Investigations carried out in our own laboratories have been aimed at elucidating the effect of varying physical and chemical properties of the bleaching earth on the quality of bleached and deodorized oils. By comparison with other

possible materials we intend to demonstrate the unique properties acid activated montmorillonites have for this application.

Although of general relevance to the processing of virtually all triglyceride oils, particular reference is made to the physical refining of palm oil products.

### EXPERIMENTAL PROCEDURE

#### Bleach Test

Evaluation of bleaching earths was made using a modified version of the SCOPA test. Palm oil samples were subjected to degumming, earth bleaching and heat bleaching. The conditions used in each stage are given in Table I. The test procedure was done in stirred glass flasks, with a nitrogen purge during stages 1 and 2 and a vacuum during stage 3. The bleached oils were filtered before and after stage 3.

We have found this test procedure to give results comparable to laboratory steam deodorization, particularly when ranking a series of bleaching earths for performance by measuring heat bleached color. For simplicity, we refer in the following tables to these colors as deodorized colors. One reservation we have for this test method is that in the absence of steam, peroxide values of zero are not obtained. The method does have advantages in ease of operation when testing a large number of earth or oil samples. We find no improvement in final color by inclusion of steam.

Heat bleached colors were measured in 5/4" cells using a Lovibond Tintometer.

## FUNCTION OF BLEACHING EARTHS

TABLE I  
Experimental Details of Laboratory Physical Refining

Stage	Degumming	Bleach	Vacuum/heat bleach
Temperature (C)	0.15%, 10% H <sub>3</sub> PO <sub>4</sub> 75	1% earth 95	— 260
Time (mins)	15	30	30

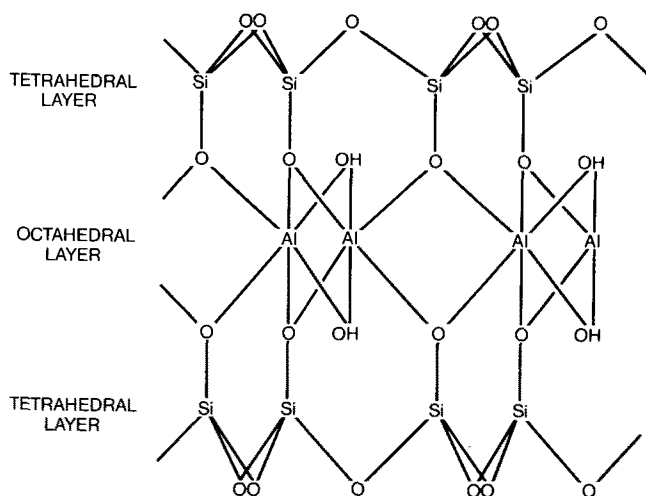


FIG. 1. The crystal structure of montmorillonite.

### Phosphorus Content

The phosphorus content of crude and refined oils was determined by X-ray fluorescence using a Phillips PW140 System. This technique (to be published) gave results comparable to those obtained by carbon furnace atomic adsorption (3), but has the benefit of requiring less sample preparation.

### Transition Metals

Copper and iron were determined by standard methods of carbon furnace atomic adsorption using organometallic standards (4).

### Surface Area and Pore Size Distribution

Surface areas were determined using a Strohlein surface area apparatus. Adsorption/desorption isotherms were measured by Coulter Electronics Ltd. using a Micromeritics Digisorb 2600. The computer facility of this instrument confirmed surface area and generated pore size distribution data.

### Electron Microscopy

Transmission electron micrographs were recorded using an Hitachi H900.

### Modifying the Physical Properties of Bleaching Earth Structure

We begin by considering the structure of montmorillonite clays and how this structure is modified during processing.

The montmorillonite crystal (Fig. 1) is a 3-layer smectite mineral consisting of two layers of silica tetrahedra separated by one layer of alumina octahedra. Some silicon ions in the tetrahedral layers have been replaced by aluminum ions and some aluminum ions in the octahedral layer have been re-

placed by ferrous, ferric, calcium or magnesium. These replacements leave a negative charge on the crystallite surface, which is neutralized by positive ions such as Ca<sup>++</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup> and H<sup>+</sup>, these ions being known as exchangeable cations. The total exchangeable ion capacity is usually in the range of 80 to 100 milliequivalents/100 g for a dry montmorillonite clay of acceptable purity.

### Acid Activation

The activation of montmorillonite with mineral acids serves three purposes:

- It dissolves the impurities such as calcite (calcium carbonate) associated with the clay in its natural state.
- It replaces the exchangeable Ca<sup>++</sup> ions on the clay with H<sup>+</sup> ions.
- It dissolves some aluminum ions out of the tetrahedral layers and some ferrous, ferric, aluminum and magnesium ions out of the octahedral layer.

The degree of acid attack during the acid activation is carefully controlled by Laporte to ensure that major structural collapse of the montmorillonite does not occur, and yet proceeds to give optimum adsorption properties.

First we will discuss the physical changes occurring during this process and how they influence the bleaching properties of the clay. The changes taking place may be examined visually by Transmission Electron Microscopy.

The transmission micrographs of the Ca<sup>++</sup> montmorillonite clay before and after acid activation show the layer structure of the montmorillonite which can be seen as dark, closely-spaced lines.

The darker lines represent the three layers of silica-alumina-silica and the space between them; the basal spacing between 9.5Å and 15.5Å depends on clay type. A more accurate measurement of basal spacing may be made by X-ray diffraction analysis (5). This spacing is found to be between 14.5 and 15.5Å for Ca-montmorillonites and 10.6Å for acid treated clays.

During acid activation, the major change in physical appearance has occurred at the edges of the platelets. The layers take on the appearance of bundles of used bank notes. Certainly, the structure remains "tight" toward the middle of each platelet with the layers separating toward their edges. These changes result in a generally more diffuse appearance for the acid treated clay.

### Pore Structure

The physical changes in structure may be examined quantitatively by determination of nitrogen adsorption/desorption isotherms, from which surface area and pore volumes are calculated.

An adsorption/desorption nitrogen isotherm for Ca<sup>++</sup> montmorillonite clay is shown in Figure 2. This isotherm corresponds to a surface area of 70m<sup>2</sup>g<sup>-1</sup>, typical of montmorillonite, which can occur in the range 50 to 120m<sup>2</sup>g<sup>-1</sup>. Note the hysteresis occurring during the desorption cycle. This type of hysteresis loop is predicted for a capillary system consisting of a combination of slit-shaped and wedge-shaped capillaries with a closed edge. A pore structure such

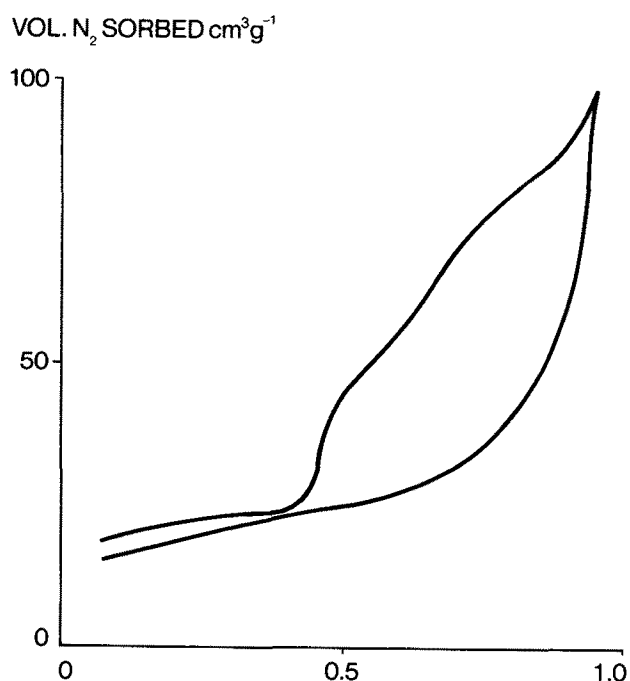


FIG. 2. Adsorption/desorption isotherm for  $\text{Ca}^{++}$  montmorillonite clay.

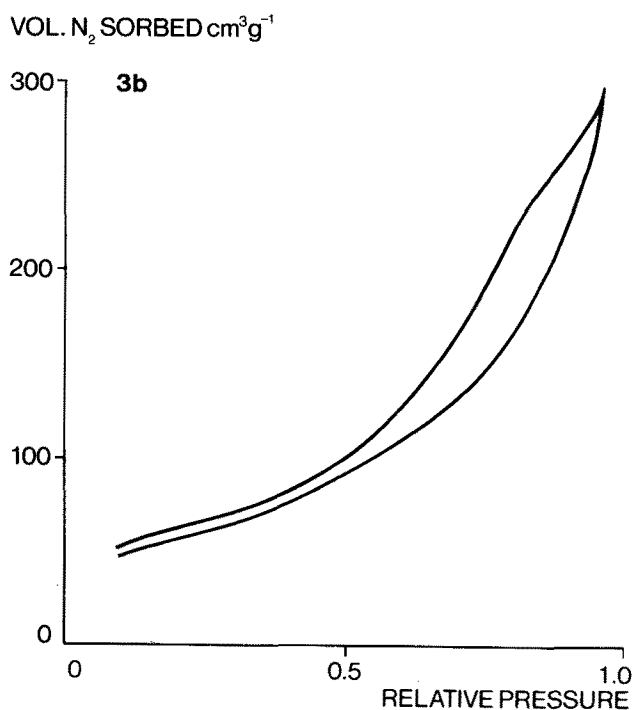


FIG. 3. The nitrogen adsorption/desorption isotherm of acid treated montmorillonite.

as this is often found for clay-type catalysts (6). The same clay when acid activated gives a nitrogen isotherm as shown in Figure 3. The total volume of nitrogen adsorbed is three times greater ( $313 \text{ cc g}^{-1}$  cf.  $103 \text{ cc g}^{-1}$ ) and corresponds to a surface area of  $227 \text{ m}^2 \text{ g}^{-1}$ . The isotherm also is changed in shape; in particular the degree of hysteresis is reduced, corresponding to a greater contribution to the pore structure by wedge-shaped capillaries.

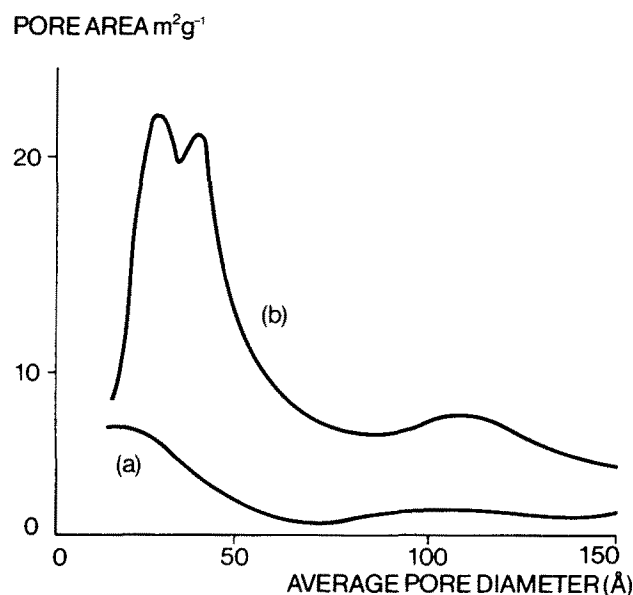


FIG. 4. The relationship between surface area and pore diameter for (a) calcium montmorillonite and (b) acid treated montmorillonite.

The changes occurring in surface area and pore type are best illustrated when converted by computer modelling into incremental pore surface distribution plots, as shown in Figure 4. The plots generated show that in natural montmorillonite the surface of the clay is in comparatively small pores of less than  $20 \text{ \AA}$  diameter. These pores correspond to the two dimensional sheets occurring between clay layers. Following acid activation, the average diameter of pores has increased and over 80% of the available surface is in pores having diameters between 20 and  $60 \text{ \AA}$ . These are pores which begin to take on a three dimensional appearance with less restricted openings.

There have been many mechanisms proposed for the nature of the adsorption process occurring during treatment of triglyceride oils with bleaching earths (7,8,9). Because of the nature of acid treated clays, it is difficult to establish the influence physical structure has upon a clay's performance as a bleaching earth and to distinguish this from the effects of chemical composition and the associated electronic effects.

Along with other workers (10) we have attempted to establish the significance of surface area to bleaching performance. We have examined laboratory samples of different surface areas where attempts have been made to keep chemical composition constant. Composition will vary to some extent since high surface areas correspond to increased aluminum dissolution from the clay structure. We were able to keep other properties constant. These include free acidity, particle size and moisture content. The clay samples produced were evaluated by use of the physical refining test described in the experimental procedure.

The Lovibond Tintometer colors obtained following heat bleach for an average quality Crude Palm Oil (Table II) processed with five laboratory-prepared activated montmorillonites of different surface area are shown in Figure 5. As predicted, deodorized color is best for the clay of greatest surface area, but reaches a peak at approximately  $260 \text{ m}^2 \text{ g}^{-1}$ . The pore size distribution for three of these samples also was determined and is shown in Figure 6. The pore frequency within the 20 to  $50 \text{ \AA}$  diameter range is greatest for samples of highest surface area. The pore size distribution of 6c has a considerable proportion of the available surface area occurring in pores above  $60 \text{ \AA}$  diameter.

## FUNCTION OF BLEACHING EARTHS

These larger pores are less efficient in the adsorption process and account for the decrease in refining performance. Surface area continues to rise with increasing severity of acid treatment until a maximum occurs beyond which surface area and bleaching performance fall progressively. The maximum surface area achievable varies from one natural montmorillonite deposit to another, but typically is in the range of 200 to 400 m<sup>2</sup>g<sup>-1</sup>. In general, the optimum bleaching properties are found in clays below the maximum surface area achievable.

Due to the nature of acid attack, individual clay particles are not homogenous in chemical composition. Qualitative EXAFS analysis shows that the edges of particles are silica rich. The contribution of this aluminum deficient structure to surface area and bleaching activity may be demonstrated. If an acid-activated montmorillonite is treated with dilute sodium carbonate, silica present only in the form of silica gel is dissolved from the particle. Following acid washing to remove excess soda and to re-exchange the clay back to the H<sup>+</sup> form, the surface area drops from 260 m<sup>2</sup>g<sup>-1</sup> to 100 m<sup>2</sup>g<sup>-1</sup>.

The bleaching performance of this clay similarly is reduced to approximately 20% of that of the original acid-activated montmorillonite.

If we now examine results obtained from a second series of laboratory activations of a montmorillonite from a different deposit (Fig. 5), we see that despite having considerably greater surface area, the bleaching performance is at best only comparable. This is a common feature when examining clays from various deposits throughout the world. Surface

area is only a useful guide to activity when comparing a range of products prepared from the same deposit using similar process conditions.

## Particle Size

The second major physical parameter affecting bleaching earth performance is particle size distribution. Three clays produced from the same source, and in all other respects identical, have particle size distributions as shown in Figure 7. The results obtained when processing Crude Palm Oil with these three clays are shown in Table III. The difference is equivalent to a total of 0.8 Lovibond Red units from coarse to fine. In general, finer clays produced by increasing the degree of milling during production give low bleached and deodorized colors. We all are aware of the need for efficient filtration, short filtration times and minimization of oil retention on the filter cake.

Several tests have been developed to rank bleaching earths in order of ease of filtration, and by these methods sample B is acceptable while sample A is too fine and would create severe problems at the filtration stage. It is found that poor control of particle size distribution is particularly detrimental to filtration. By careful control during several production stages, acceptable filtration performance is obtained without diminishing bleaching performance.

## Clays of Related Structure

The ability of montmorillonite to undergo development of an increased surface area is almost unique in mineralogical

TABLE II

Characterization of Crude Palm Oil and Palm Stearin Used in Bleaching Earth Evaluation

	Crude palm oil	Crude palm stearin
Color	22R (1" cell)	18R (1" cell)
Free fatty acid	3.7%	4.0%
Phosphorus (ppm)	10	23
Iron (ppm)	3	6
Anisidine value	8	10
Peroxide value (m.e.qkg <sup>-1</sup> )	6	5

LOVIBOND RED 5¼" CELL

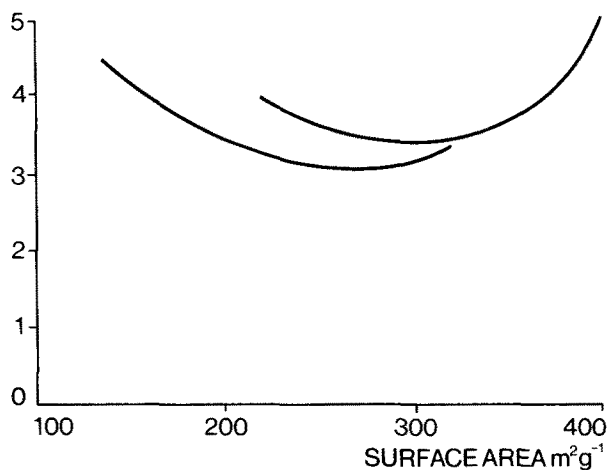


FIG. 5. The relationship of deodorized palm oil color to bleaching earth surface area for laboratory acid activated montmorillonites from two different deposits.

PORE AREA m<sup>2</sup>g<sup>-1</sup>

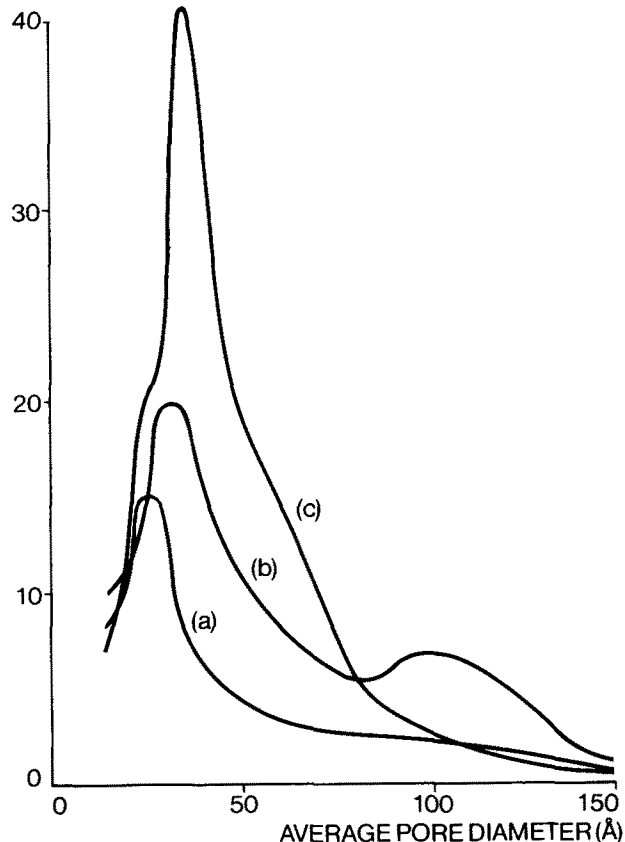


FIG. 6. Incremental pore surface area against average pore diameter for laboratory activated montmorillonites of surface area (a) 131 (b) 259 and (c) 316 m<sup>2</sup>g<sup>-1</sup>.

terms. Other commonly occurring clay minerals such as kaolinites and micas do not have this potential to increase surface area on acid treatment. Many other layer lattice clays related to montmorillonites have been examined by ourselves and other workers as adsorbents (12,13) and more

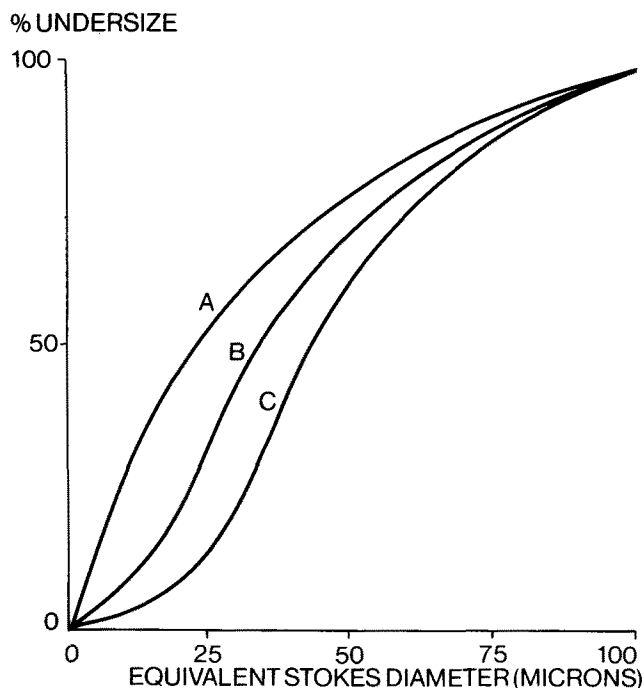


FIG. 7. Particle size distribution of laboratory milled bleaching earths.

TABLE III

Lovibond Colors of Physically Refined Palm Oil Using Laboratory Milled Bleaching Earth

Clay sample	Lovibond color 5¼" cell	
	Y	R
A	25	2.3
B	28	2.6
C	30	3.2

TABLE IV

Lovibond Colors of Physically Refined Palm and Palm Stearin Using Naturally Occurring and Synthetic Materials with Increasing Surface Area

Bleaching material 1% clay	Surface area m <sup>2</sup> g <sup>-1</sup>	Crude palm oil Lovibond		Crude palm stearin Lovibond	
		Y	R	Y	R
Mica (muscovite)	< 5	35	3.0	60	6.8
Kaolin	6	50	5.0	60	10.6
Perlite	15	35	3.4	60	6.8
Natural montmorillonite	60	55	5.5	70	10
Natural montmorillonite	140	30	2.8	60	7
Fulmont AA <sup>a</sup>	170	20	1.7	45	3.2
Florisil <sup>b</sup>	298	40	4.5		
Laponite <sup>a</sup>	350	20	2.0	55	5.0

<sup>a</sup>Fulmont AA and Laponite are trademarks of Laporte Industries Ltd.

<sup>b</sup>Florisil is a trademark of the Floridin Company.

specifically as potential bleaching earths, in either their natural state or following some form of activation. To date none has found anything other than limited commercial application. For instance, naturally occurring clays having a montmorillonite content which, either through the nature of deposition or by a natural weathering process, display limited adsorption properties. However, they are generally poorer in performance when compared to acid-activated clays.

We must be careful at this point to distinguish between bleaching activity and potential as an adsorbent for use in edible oil refining. This is particularly true for palm oil and its derived products which, due to their high carotenoid content, are apparently easily decolorized during the deodorization stage of physical refining. Several minerals have been claimed to give bleached colors comparable to activated montmorillonites, but subsequent deodorized colors are poor. Because they possess little or no adsorption ability they are unable to assist in the removal of pigment decomposition products, metal impurities or phosphatides. The deodorized colors obtained on refining crude palm oil and crude palm stearin with a range of natural clays are shown in Table IV. Results obtained using an activated clay Fulmont AA are included for comparison. Final refined colors are particularly poor for palm stearin when using natural clays.

Table IV also includes results obtained on two synthetic adsorbents, both of high surface area. Laponite, a synthetic hectorite with a surface area of 350m<sup>2</sup>g<sup>-1</sup>, is closest to montmorillonite in structure and is an efficient bleaching earth. Florisil, a magnesium silicate, also is of high surface area (ca. 300m<sup>2</sup>g<sup>-1</sup>) but from our work does not possess adequate bleaching performance. The differences displayed by these materials serve to emphasize that high surface area is not the only prerequisite for a bleaching earth.

#### Modification of Chemical Composition

During any investigation of the chemical properties of adsorbents which influence their bleaching ability, it is difficult to separate the many contributing factors. These include chemical composition before and after acid activation, clay acidity and water content. Despite these problems, much work has been carried out in this area.

#### Cation Composition

As already described, montmorillonites have exchangeable cations at their surface. It has been shown that variation of these exchangeable cations alters the adsorption isotherms for the pigment  $\beta$ -carotene.

It is demonstrated that for a comparable level of exchange, the activity of the various cation-exchanged clays are in the order of  $Mg^{++} > H^+ > Ca^{++} > Na^+$  (14). We have found in our own work with cation exchanged forms of Fulmont Premiere when bleaching soybean oil  $Al^{+++} \sim H^+ > Ca^{++} > Na^+$ . When physically refining palm oil the differences in deodorized color from  $Al^{+++}$  to  $Na^+$  are less than 0.2 Lovibond red values.

It is suggested that the  $\beta$ -carotene molecules can either be adsorbed directly onto a cation to form a chemisorbed complex which then undergoes further reaction or react directly with the protonic centers present on the clay surface. If metal cations interact with the  $\beta$ -carotene molecule, the activities of these cation exchanged clays may be expected to be inversely proportional to their ionic radii as their electrostatic fields increase. Alternatively, the metal ions may induce dissociation of chemisorbed water, resulting in the production of Brönsted acid centers. It is likely that both reactions occur on the surface and are influenced by the nature of this surface.

#### Bleaching Earth Acidity

A bleaching earth exhibits the properties of a solid acid behaving as a proton donor (Brönsted acid) or electron acceptor (Lewis acid). The acid strength of a clay is determined in non-aqueous solution by titration with a base, usually *n*-butylamine, in the presence of indicators effective at specific acid strengths (15). No direct correlation has yet been found between bleaching performance and surface acidity. The acid strengths of acid activated montmorillonites fall into a narrow range, particularly when compared to differences between the natural montmorillonite ( $H_0 > -3$ ) and acid treated clay with ( $H_0 > -5$ ). It should be emphasized that bleaching earths produced from acid activation of montmorillonite regardless of process differences such as type of mineral acid employed will have a  $SiO_2 - Al_2O_3$  surface with essentially similar acid strength unless specific attempts have been made to reduce this acidity. It is the acidity of the clay surface which contributes to activity and also to potentially detrimental properties such as free fatty acid (FFA) formation and isomerization of the triglyceride alkyl chain.

The latter is prevented and controlled by avoidance of extreme processing conditions, particularly high temperatures during the bleaching stage. A rise in FFA frequently is ascribed to high free acidity on the clay. We have examined bleaching earths from several sources including our own range of products and found extreme difficulty in detecting substantial rises in FFA even under exaggerated conditions of increased earth dose and long contact time. We have found the temperature to be the major process variable affecting the increase in FFA. Figure 8 shows the FFA of palm oil when bleached with increasing earth dosage levels at 100 C and 150 C. At 100 C FFA increased by 0.1% up to earth levels of 2% and to a maximum using greater than 5% earth. At 150 C FFA increased steadily and still was rising with 8% bleaching earth.

It must be accepted by bleaching earth manufacturers that a rise in FFA can occur during the bleaching process. Bleaching earths are required to perform the dual role of adsorbent and catalyst in the bleaching process, and both are dependent on the acidity of the clay. It is possible to reduce this acidity, for example by ion exchange with sodium, but not without a resulting loss in bleaching activity. Fortunately, applications which are particularly critical to FFA rise such as margarine manufacture and alkali refining do not demand the most active clays.

Synthetic zeolites have been examined for their ability to adsorb fatty acids (16). Sodium Y-zeolite is the most

efficient for this application. However, the practicability of use may be questioned because of high cost. Second, the zeolite is adsorbing only FFA already present or formed during the bleaching stages and not reducing the generation of fatty acid. An adsorbent for FFA may have application during alkali refining but is unlikely to be of great benefit in physical refining of palm oils.

The production of oil with acceptable oxidative stability requires similar careful control of refining process conditions. Few problems are encountered when the bleaching temperature remains below 130 C and steps are taken to reduce air oxidation. Peroxide values for deodorized oils are  $< 1 \text{ meq/kg}^{-1}$  and anisidine values are of the order 2 to 3. If bleaching is done at 150 C, anisidine values (AV) begin to rise (Table V). Oxidative stability appears not to be damaged by increased earth dosage levels. In fact, for very poor crude palm and palm stearins higher dosage levels reduce AV during the bleaching process (Table VI).

It has been demonstrated that the colored pigments in good quality crude palm oils have molecular weights less than the triglycerides present (17). During bleaching these low molecular weight components are removed from the oil to varying degrees. The coloring components of the deodorized oil are found to have molecular weights greater than triglycerides. They are formed by polymerization of low molecular weight precursors during high temperature

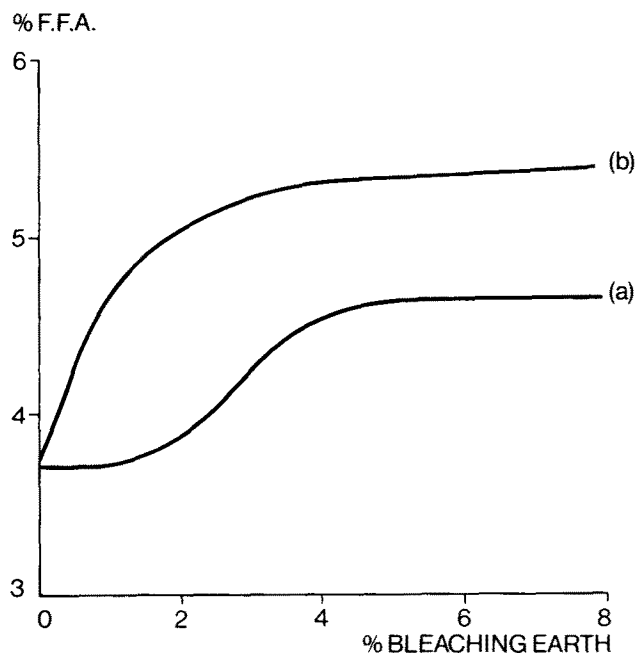


FIG. 8. The free fatty acid content of palm oil (FFA = 3.7%) bleached at (a) 100 C and (b) 150 C.

TABLE V

The Effect of Bleaching Temperature on the Anisidine Values of Bleached and Deodorized Crude Palm Oil when Bleached with 1% Fulmont AA

Temperature C	AV
95	2
110	3
130	6
150	13

TABLE VI

The Effect of Earth Dosage on the Anisidine Value of Crude Palm Stearin when Bleached with Fulmont AA at 95 C

% Earth dose	AV
—	12
1	8
2	6.1
3	4.7

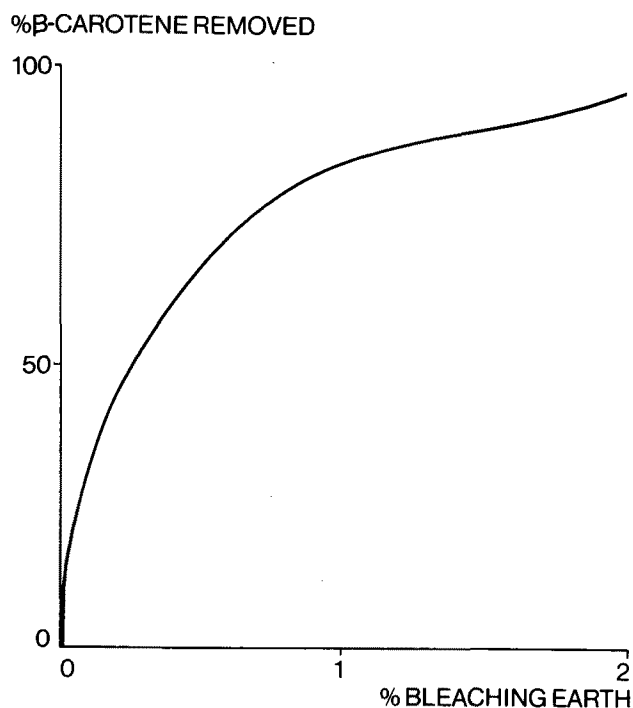


FIG. 9.  $\beta$ -Carotene content of palm oil when bleached at 90 C for 30 min with Fulmont AA.

TABLE VII

The Copper and Iron Content of Degummed (0.15 wt%  $H_3PO_4$ ) and Bleached Palm and Palm Stearin, when Bleached with Laboratory Activated Earths of Surface Area

	% Earth dose	Fe (ppm)	Cu (ppm)
Crude palm oil			
Crude oil	—	2.7	0.35
Bleaching earth <sup>a</sup>	0.5	0.32	0.16
	2.0	0.11	0.08
	3.0	0.09	0.06
Bleaching earth <sup>b</sup>	1.0	0.3	0.14
Crude palm stearin			
Crude oil	—	2.4	0.24
Bleaching earth <sup>a</sup>	1.0	0.9	0.07
	3.0	0.12	0.04
Bleaching earth <sup>b</sup>	1.0	1.7	0.15

<sup>a</sup>200 m<sup>2</sup>g<sup>-1</sup>.

<sup>b</sup>130 m<sup>2</sup>g<sup>-1</sup>.

deodorization. High molecular weight components also have been found at variable levels in crude palm oils and

may be the result of damage occurring subsequent to harvesting. The possibility that these compounds are natural products cannot be excluded.

We have shown that during acid activation montmorillonite undergoes considerable changes to its chemical composition and physical structure. A clay is formed of high surface area and the correct chemical composition at the surface to preferentially attract pigment molecules of molecular weights lower than the triglyceride oil. For example, the  $\beta$ -carotene content of crude palm oil is reduced during bleaching with increasing earth dosage as demonstrated in Figure 9. It is not unreasonable to propose that bleaching earths remove other related low molecular weight components in a similar fashion. These are pigments which, unlike  $\beta$ -carotene, thermally decompose to give colored high molecular weight components in the deodorized oil. This assumption is supported by the use of other bleaching materials which give similar bleached colors to activated earths but on subsequent deodorization produce darker deodorized oil as shown in Table IV. The dependence of final deodorized color on bleaching ability is difficult to demonstrate with palm oil since the major coloring component,  $\beta$ -carotene, is present in high levels and masks other coloring components.

The removal of other impurities, such as transition metals, (copper and iron), soaps and phospholipids, occurs we believe by a mechanism similar to that for pigment removal and is dependent on surface activity. The transition metal contents of several bleached oils are shown in Table VII. They are clearly dependent on bleaching earth dosage and surface area.

The acid treatment of montmorillonite clay produces a specialty adsorbent from a naturally occurring mineral. During this process, the physical structure and chemical composition are altered in a controlled way to maximize specific properties. An efficient bleaching earth is produced having a surface of the correct chemical composition and pore distribution selectively attractive to the detrimental components of crude triglyceride oils.

The removal of colored pigments is a common, simple visual guide, often mistakenly used to gauge the overall performance of a bleaching earth. However, the ability to remove other undesirable impurities is less readily apparent. The choice of the correct bleaching earth to use in any specific application must take into consideration removal of all undesirable impurities in addition to color. It is in this area where fully developed bleaching earths can greatly benefit the refiner.

Other synthetic and some natural materials possess properties similar in some aspects, but without exception, fall short as competitive adsorbents for this demanding application.

Research continues to keep pace with new developments occurring within your industry, to overcome technical problems in bleaching earth application and also to improve their performance. Other materials will continue to be evaluated for possible application as bleaching earths. At present, however, the unique properties of acid-activated montmorillonites prove the best combination of technical performance and cost effectiveness to the edible oil refiner.

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## The Physical Refining Process

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### ABSTRACT

This paper deals with influences and optimizing of changing process conditions for physical refining of palm oil. These process variables are temperature, pressure, residence time, fluid flow and stripping steam to oil ratio. These parameters influence not only finished oil quality, oil yield, energy consumption and running costs, but also content and yield of natural stabilizers like tocopherols or color compounds like carotenes, and last, but not least, environmental load of waste water and exhaust air as studied under industrial plant conditions. With the right pretreatment process physical refining of palm oil is not only much more economical than chemical refining in connection with stripping steam deodorization, but also causes much less pollution by waste water and exhaust air.

Under all these aspects the performance of continuously operated industrial plants now in use for physical refining of palm oil is being examined. Because of the water solubility of the low-boiling thermal degradation products, the effluents of nearly all installations must be specially treated to fulfill today's legal requirements on BOD and on COD as well as on oil and grease content. The only exception is a new counter-current two-step film type physical refining process in connection with a combined sophisticated steam ejector vacuum and two-step exhaust air washing system, with which, without any air pollution, COD values of <50 for waste water are possible.

For best oil quality deacidification should be done with pressure drop of less than 1 torr at 2 to 3 torr tap pressure at 260 C working temperature with residence times of 10 min and counter-current exchange efficiency of 6 to 8 theoretical plates.

### PHYSICAL REFINING-DISTILLATION PROCESS

Physical refining of vegetable oils is a distillation process (1-3) in which, under low absolute pressures of 2 to 10 torr and high temperatures of 240 to 270, the accompanying lower boiling compounds are distilled off from the fatty acid triglycerides—the main components of the oils—by using unsaturated open steam as the effective stripping agent (1). The byproducts consist mainly of free fatty acids and such degradation products as hydrocarbons, methylketones and aldehydes. The temperature-pressure relationship for oils and some of the main byproducts are shown in Figure 1. According to our comparative evaluation of these data the mixture stearic acid-tristearin can be considered a good model for calculating necessary separation power in physical refining and distillative deodorization of edible oils (1).

### SPECIAL SEPARATION CONDITIONS OF PHYSICAL REFINING FOR PALM OIL

Palm oil and other vegetable oils contain, beside fatty acid triglycerides, a large number of other constituents in low concentrations, some only in ppm or even ppb. Among these are free fatty acids as main components in concentrations

up to several percent. In much smaller contents are pigments, stabilizers, various flavor and odor compounds, as well as products formed by autoxidative and/or heat decomposition of peroxides, pigments and natural stabilizer compounds. According to newer published results Malaysian crude palm oil on average can be characterized by the data in Table I (4-7).

In physical refining not only are the mentioned undesired low-boiling byproducts like free fatty acids, aldehydes, ketones and hydrocarbons stripped off by open steam, but parts of higher-boiling special stabilizer compounds like tocopherols and sterols are carried over into the distillate phase. In such mixtures tocopherol compounds with molecular weights of only 421 will act against triglycerides of  $C_{16}/C_{18}$ -fatty acids with molecular weights of 800 to 850, causing separation factors  $\alpha$  between 50 and 200. By the necessary stripping steam amount of normally 1.5 to 2.5% used in this process at temperatures of above 250 C and pressures between 2 and 8 torr, not only the low boilers but also such stabilizer compounds will go more or less into the distillate.

### INFLUENCE OF METALS IN RELATION TO WORKING CONDITIONS ON NATURAL STABILIZER CONTENT (8-23)

According to the data in Table II (4), the tocopherol loss in installations for physical refining can be up to 44.5%, while in steam deodorization after chemical refining these losses are below 10%. The reason for the different behavior in processing when using practically the same technical installations has to be seen in decisive lower values for temperature, residence time and open stripping steam amount. In nearly all physical refining installations the product hold-up times at temperatures above 250 C and pressures between 2 and 8 torr with open steam amounts of 2 to 3% will normally be kept in the range of 2 to 3 hours. For steam deodorization in these installations at the same temperature and pressure working conditions, residence times of only 1 to 2 hours are needed, with open steam consumptions of 1 to 2% at lower temperature profiles.

These results are in full agreement with our open observations (24) that the tocopherol loss can be markedly diminished by using a counter-current film process. The installation is working at pressures of 2 torr, temperatures not higher than 260 C with residence times above 230 C of below 20 min including heating and cooling periods and open steam amounts of less than 0.6% of oil throughput. The layout has to be made so that under working conditions the pressure drop between top and bottom of the two or three film columns is below 1 torr. Because of the high